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A REVIEW OF EXPERIMENTAL MEASUREMENT  
METHODS BASED ON GAS-PHASE CHEMILUMI-  
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Arthur Fontijn, et al

Purdue University

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# PROJECT SQUID

## TECHNICAL REPORT AC-12-PU

### A REVIEW OF EXPERIMENTAL MEASUREMENT METHODS BASED ON GAS-PHASE CHEMILUMINESCENCE

BY

ARTHUR FONTIJN  
DAN GOLOMB  
JIMMIE A. HODGESON

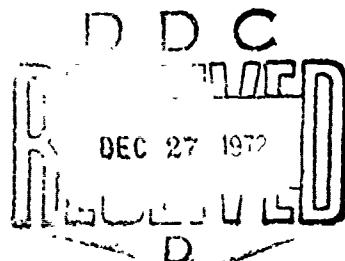
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BASED ON GAS-PHASE CHEMILUMINESCENCE

by

ARTHUR FONTIJN  
AEROCHEM RESEARCH LABORATORIES, INC.

DAN GOLOMB  
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES

JIMMIE A. HODGESON  
ENVIRONMENTAL PROTECTION AGENCY

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III

## ABSTRACT

Measurement methods based on gas-phase chemiluminescence have found extensive use in a wide variety of disciplines such as homogeneous and heterogeneous reaction kinetics, thermochemistry, gas dynamics, aeronomy, analytical chemistry and air pollution (source and ambient atmospheric monitoring). Chemiluminescence intensity measurements are used to determine reactant and/or product concentrations from which are derived rate coefficients, diffusion coefficients, densities, wall recombination coefficients and heats of formation. Such measurements also allow temperature determinations. Additionally, chemiluminescence flow visualization is used for the testing of mathematical flow models and the measurement of atmospheric mass transport. In this review the various methods and reactions are discussed in the context of their specific applications.

## A REVIEW OF EXPERIMENTAL MEASUREMENT METHODS BASED ON GAS-PHASE CHEMILUMINESCENCE

Arthur Fontijn<sup>†</sup>

AeroChem Research Laboratories, Inc., P.O. Box 12,  
Princeton, N.J. 08540

Dan Golomb

Air Force Cambridge Research Laboratories, L.G. Hanscom  
Field, Bedford, Mass. 01730

Jimmie A. Hodgeson

Environmental Protection Agency, Technical Center,  
Research Triangle Park, N.C. 27711

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## I. INTRODUCTION

The first application of gas-phase chemiluminescence could have been the contribution to the illumination of a cave by the blue portion of a wood flame. Qualitative flame analysis has been in use since at least the 16th Century.<sup>1</sup> For many present-day applications, observation of chemiluminescence has the advantages that (i) measurement of such radiation in no way interferes with the reacting environment, (ii) the measuring tool does not have to be exposed directly to the active reaction environment, i.e. remote sensing is possible, (iii) transient species can be readily identified and (iv) in its most elementary form the observer's eye is the only tool required. For these reasons chemiluminescence measurements represent an obvious and often immediately available method for investigating a given medium. When coupled with modern reliable sensitive detection methods, which cover the optical spectrum from the vacuum ultraviolet through the near infrared, chemiluminescence provides a major tool for species concentration measurements. Chemiluminescence measurements are also used in studies of homogeneous reaction kinetics, thermochemistry, gas-surface interactions, temperatures of reaction environments, atmospheric mass transport, and gas dynamics.

It is the purpose of the present paper to summarize these various methods and to discuss them in the context of the environments to which they have been applied, in the expectation that such a juxtaposition of knowledge from different disciplines and research areas can lead to further useful developments based on chemiluminescence. While many examples pertaining to specific species and reactions will be given, these are not intended to include all such observations but rather to illustrate the methods being discussed. To further delineate the scope of this review, two definitions are in order (i) chemiluminescence is the emission of radiation from a chemi-excited species and (ii) chemi-excitation is a process by which excited species are formed as a direct result of the formation of new chemical bonds. Thus radiation following collisional excitation (e.g.  $A + B + \text{kinetic energy} \rightarrow A + B^*$ )--a principal radiation source in high temperature reaction environments, or dissociative reactions (e.g.  $AB^+ + e^- \rightarrow A^* + B$ ), or radiation resulting from charged species impact or the absorption of radiant energy (e.g. fluorescence) will not be considered. Emphasis is placed on optical emission measurement methods which are specifically based on chemiluminescence.

From the above definition a formalized description of chemiluminescence may be written as:



By virtue of the implied occurrence of a chemical reaction chemiluminescence measurements thus often have the important characteristic that the species being observed is a reaction product and not a reactant. However, since processes such as



followed by light emission are also examples of chemiluminescence this does not always apply. In reactions such as (3)  $C^*$  may be formed directly in an excited state or be excited by collisions with  $AB^*$ . We will refer to the latter case as indirect chemiluminescence.

Chemiluminescence measurement methods have found their widest variety of uses in the laboratory. Most methods for applied usage have been derived from laboratory methods and more such methods await application. Laboratory methods and their limitations are discussed in Section II. The newest, most rapidly growing field of gas-phase chemiluminescence application is pollutant monitoring. Air or exhaust gases are continuously sampled and the concentration of a selected pollutant is determined from the intensity of the chemiluminescence produced by its reaction inside a monitor; these methods are discussed in Section III. Releases of chemical tracers leading to artificial upper atmospheric chemiluminescence are a very practical, relatively inexpensive means for studying that environment; the status of this area and that of natural airglows is reviewed in Section IV.

## II. LABORATORY METHODS

### A. Elementary Processes at Moderate Temperatures

Chemiluminescence is a widely used indicator in titration reactions of many atomic and free radical species in tubular fast-flow reactors. Such reactors have been used mainly in the 200 to 750 K regime. (For a description of their use see e.g. Refs. 2-4.) The technique may be illustrated by the air afterglow reaction:<sup>2,5</sup>



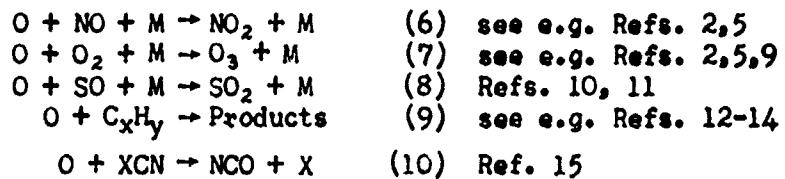
O atoms at a fixed point in the reactor are titrated by addition of  $NO_2$  via the fast reaction



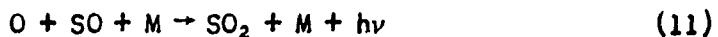
When the (volume) flow of  $NO_2$  is less than that of the O atoms, NO is produced in the presence of O and the whitish-green glow from Reaction (4) is observed. However, when the flow of  $NO_2$  equals or exceeds that of O no O atoms are present downstream from the  $NO_2$  inlet and the glow contracts to the small mixing region surrounding the nozzle. The important requirement for a titration reaction is that it be fast and complete near the titrant inlet. The indicator reaction should be slow so that it can be observed downstream from

the inlet. Other methods besides chemiluminescence can be used to follow the titration reaction, e.g. mass spectrometric determination of the  $\text{NO}_2$ -consumption plateau<sup>6</sup> and E.P.R.<sup>7</sup> or optical absorption measurements<sup>8</sup> of the O-atom disappearance. These methods have confirmed the validity of the chemiluminescence measurements but generally require a more elaborate experimental set-up. It is useful to keep in mind that in the sequence of Reactions (5) and (4) chemiluminescence is used as the indicator reaction not as the titration reaction, contrary to an unfortunately rather common misuse of terms.

Indicator reactions are also used to measure the change in reactant concentration with time obtained from the distance along the reactor and the average gas velocity. If a trace of NO is present in or added to an atomic-O flow, the relative intensity of the air afterglow is a measure of the relative  $[O]$ , since the combination of Reactions (4) and (5) results in recycling of NO and hence a constant  $[NO]$ . Examples of quantitative kinetic studies in which the O-atom consumption rate has been determined in this manner include



in which  $X = H, Cl, Br$ . While consumption of NO by free radicals does not seem to have interfered with measurements in O/hydrocarbon systems (Reaction 9), NO is known<sup>16</sup> to be a very efficient free radical scavenger and some caution in the use of the air afterglow in such a reaction system is necessary. Reactions (8) and (10) serve to illustrate uses of chemiluminescence in the measurement of free radicals and reaction products. Reaction (8) is accompanied by emission of the  $SO_2$  afterglow



By simultaneously measuring the relative intensities of both the O/NO and O/SO afterglows a measure of the consumption of both O and SO is obtained.<sup>10,11</sup> Reaction (10) is followed by:



i.e. by NO production. By adding known small flows of NO to the O/XCN mixture and plotting the air afterglow intensity versus NO flow, a negative intercept on the abscissa (NO flow axis) is obtained, the magnitude of which directly yields the NO-production rate.<sup>15</sup>

Absolute concentrations can also be obtained from the relative air afterglow intensity. This requires that the detector (photo-multiplier plus light filter or monochromator) output be calibrated in terms of  $[O][NO]$  for a given reactor/detector geometry and that the absolute concentration of one of these reactants be known. This approach has been found useful in static reactors in which the  $NO_2$  titration because of its flow nature cannot be carried out,<sup>17</sup> in systems in which ground state O atoms are produced (such as by quenching of singlet excited O atoms)<sup>18</sup> and where flow metering of  $NO_2$  is found to be inconvenient.

Fontijn, Meyer and Schiff<sup>19</sup> (FMS) have accurately measured the absolute rate coefficient for light emission of the air afterglow reaction,  $k_4$ , together with the spectral distribution of the glow, which is a continuum extending from 388 nm well into the infrared. This glow is commonly used as a secondary standard for absolute quantum yield determinations of light emitting processes in the gas phase. The relative intensity emitted in a given wavelength region by the investigated process need only be compared to that of the O/NO reaction using the same conditions of geometry and optics. Fontijn and Lee<sup>20</sup> have extended such comparisons to the liquid phase and found good agreement with the common liquid-phase (luminol oxidation) chemiluminescence light intensity standard. A check on  $k_4$  by Vanpee et al<sup>21</sup> also gave good agreement, but subsequent work on the spectral distribution<sup>21-23</sup> has shown deviation from the FMS data in the (infra)red, though excellent agreement exists for  $\lambda \leq 650$  nm. For quantum yield measurements above 650 nm it would be best to use a combination of the FMS data below 650 nm with the more recent ir spectral distribution measurements. Stair and Kennealy<sup>23</sup> have shown the emission to extend to at least 3700 nm. Since the O/NO continuum does not extend below 388 nm, it cannot be used directly as a standard for that wavelength region. However, the quantum yields of other glows, which partially overlap the O/NO wavelength region, have been determined by comparison to the O/NO glow and can be used as secondary standards in the ultraviolet. In particular, the  $SO_2$  afterglow continuum<sup>11,24</sup> (Reaction 11) appears useful down to about 260 nm. Recently Mandelman, Carrington and Young<sup>26</sup> have accurately determined the absolute rate coefficient for N-atom/O-atom pre-association leading to  $NO \delta(O,O)$  emission (Reaction 16, below) near 191 nm. No standard reactions at shorter wavelengths have yet been provided.

The NO/O standard can be used directly in the 1 to 10 Torr regime, at 300 K, in an Ar or O<sub>2</sub> carrier. It must be remembered that the detailed reaction mechanism<sup>25</sup> involves participation of a third body, M, and that, as a result, the intensity depends on the nature of M and becomes [M]-dependent at lower pressures where quenching no longer competes successfully with emission. For the M-dependences of  $k_4$  see Clyne and Thrush<sup>27</sup> and Kaufman and Kelso;<sup>28</sup> for the temperature dependence see Hartunian, Thompson and Hewitt.<sup>29</sup>

The reaction



gives rise to a banded HNO spectrum in the 600-800 nm region. The intensity of this emission is<sup>30</sup> proportional to  $[H][NO]$  and the reaction has been used in H-atom studies. The titration reaction for which (13) serves as the indicator is



Subsequent rapid reactions of OH regenerate H and as a result the NO<sub>2</sub> end point flow is 1.5 times the initial H-atom flow.<sup>8,31</sup>

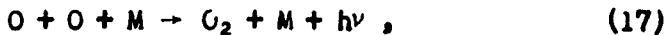
Further examples of laboratory afterglow methods may be illustrated by the nitrogen, nitric oxide and oxygen afterglows. Absolute N-atom concentrations can be determined via titration<sup>7,8,32,33</sup> with NO:



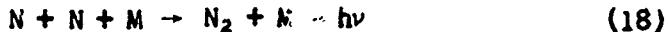
When an insufficient flow of NO is added to remove all N atoms a mixture of N and O atoms exists downstream from the NO inlet and the blue NO afterglow can be observed<sup>34-37</sup>:



When the NO flow is in excess of the N-atom flow, the downstream gases contain O and NO and the air afterglow appears again. At the end point the tube visually appears dark. However, in the ultra-violet O<sub>2</sub> Herzberg bands and in the infrared O<sub>2</sub> Atmospheric bands, both due to<sup>36-39</sup>:



can still be observed. In the nitrogen afterglow itself several band systems, due to<sup>36,37,40-44</sup>



are observed, of which the yellow First Positive Bands are most commonly used for measurements. These bands and the NO  $\beta$ ,  $\gamma$  and  $\delta$  bands can be used to follow atom concentrations. The light intensities are proportional to  $[N]^2$  and  $[N][O]$ , respectively. For rate coefficient data and restrictions of pressure see the references quoted. The temperature dependences of  $k_{16}$  and  $k_{18}$  have been measured over a wide range by Gross and Cohen,<sup>45,46</sup> (see also Campbell and Thrush<sup>34</sup>). The reader is referred to review papers by Carrington and Garvin<sup>47</sup> and by Thrush<sup>48</sup> for the detailed mechanisms of Reactions (16) to (18), as well as of several further reactions which may have potential for practical applications e.g., the O/CO glow and the halogen atom recombination afterglows.

The oxygen afterglow intensity from Reaction (17) is proportional to  $[O]^2$  and in principle can also be used for concentration measurements in O-atom reaction studies. However, both band systems are strongly forbidden (radiative lifetimes  $> 1$  sec)<sup>37,38</sup> and consequently have a low intensity. Moreover, even though quenching will reduce the effective lifetime of the emitters ( $O_2 A^3\Sigma_u^+$  and  $b^1\Sigma_g^+$  respectively), the emission in flow tubes may occur well downstream from the point of emitter formation and the intensity then will no longer be a true indication of local [O]. Radiative lifetimes of the other emitters discussed above are on the order of  $10^{-6}$  sec or less; since typical linear velocities in laboratory flow tubes are on the order of  $10^2$  to  $10^4$  cm sec<sup>-1</sup> this transport problem does not arise in their use. However, care must also be exercised with short-lived emitters, for example in the use of the  $I \propto [N]^2$  and  $\propto [N][O]$  relationships in mixtures containing a second reactant. In a few instances it has been shown that such reactants or a reaction intermediate can enhance afterglow intensities by catalytically increasing the rate of atom recombination into the emitting state. Thus,  $I_2$  addition can enhance the Lewis-Rayleigh afterglow intensity,<sup>49</sup> and  $C_2F_4$  and  $C_2H_4$  have been observed to increase the  $NO \gamma$  and  $\beta(v' \leq 2)$  intensities.<sup>50</sup> The  $NO \beta$  emission intensity also has been shown recently<sup>51</sup> to be not strictly proportional to  $[N][O]$ , due to N, O and  $O_2$  action on a precursor of the emitting  $B^3\Pi$  state. For these reasons it appears safest to use the  $NO \delta(v' = 0)$  bands, whose emitter is produced directly by a two-body pre-association reaction<sup>35,36</sup> unlike the other emissions discussed above which are produced by three-body reactions.

The nitrogen afterglow also offers several examples of the use of indirect chemiluminescence.  $N_2(A^3\Sigma_u^+)$  molecules are formed via N-atom recombination but, due to their long radiative and short chemical lifetime, these excited molecules cannot normally be observed in emission. However, when a trace of Hg is added to the flow, rapid energy transfer occurs and the resulting 253.7 nm emission can be used to monitor  $N_2(A^3\Sigma_u^+)$  and estimate its concentration.<sup>52</sup> Other  $N_2^*$  species formed in the afterglow apparently do not excite the emitter, Hg( $6^3P_1$ ).<sup>52</sup> CO( $a^3\Pi$ ) has been similarly monitored in various reaction mixtures i.e. by energy transfer to Hg and to  $NO(X^2\Pi_g)$ , leading to Hg 253.7 nm and  $NO \beta$  and  $\gamma$  band emission, respectively.<sup>53,54</sup> vibrationally excited ground-state  $N_2$  molecules can also be formed in nitrogen afterglows. Addition of  $CO_2$  leads to energy transfer and emission of the 4300 nm vibrational fundamental band of  $CO_2$ . Electronically excited species present do not produce this band. Similar observations have been made using  $N_2O$ .<sup>55</sup>

Chemiluminescence from atom reactions has also been used to determine bond dissociation energies. The general spectroscopic methods for determining bond energies have been discussed by Gaydon.<sup>36a</sup> Chemiluminescence is sometimes the preferred technique

for producing clean interpretable spectra, for example in the determination of the lower limit to the BaO bond energy from the Ba + NO<sub>2</sub> chemiluminescence in a crossed beam experiment.<sup>57</sup> Chemiluminescence measurements of changes in atom concentrations near catalytic surfaces have been employed to measure atom-surface recombination coefficients,<sup>58-60</sup>  $\gamma$ , the efficiency of catalytic probes in destroying free atoms<sup>61</sup> and atomic diffusion coefficients.<sup>58,61-63</sup> Atom-surface interactions can also give rise to luminescent surface phenomena, i.e. to candaluminescence of lumophoric substances such as CaO and MgO. The intensity of the candaluminescence associated with the impingement of N and O atoms has enabled determinations of  $\gamma$ .<sup>64-66</sup>

### B. Flame and Shock Tube Studies

Several self-sustaining flame types are known and are discussed in several texts, e.g. Gaydon and Wolfhard.<sup>67</sup> Of these premixed laminar flames are probably most widely used in present-day laboratory practice. In such flames reaction time and distance are (as in flow tubes) directly proportional to each other, which is an important advantage in (i) kinetic studies and (ii) all studies in which it is desirable to distinguish between flame zones. Two distinct major reaction zones are present in premixed flames; (i) the primary combustion zone characterized by wide departures from equilibrium and in many flames intense chemiluminescence and (ii) the burned gas zone in which equilibrium conditions are more closely approached and in which reactions of free radicals, etc., formed in the primary zone can readily be studied. Several of the atomic and radical species present in flames are identical to those discussed in the previous section and some of the same chemiluminescent reactions can be used in a similar manner. However, since flame environments usually contain a larger number of reactants, errors due to side reactions or overlapping emissions are more likely and considerable caution in the use of chemiluminescent emissions in measuring e.g. reactant-time profiles is needed. Moreover, as a consequence of the high temperature reaction environment represented by flames, emissions from other sources, particularly collisionally excited species, often dominate and background emissions may underlie some of the emissions being measured.

Distinguishing between chemi-excitation and collisional excitation is sometimes difficult and may require extensive research. Both processes can contribute to the establishment of thermal equilibrium levels of excitation. However, in systems in which collisional excitation dominates the excitation cannot exceed equilibrium levels. Hence, non- or extra-equilibrium radiation (also referred to as "suprothermal" radiation) is usually chemiluminescent in origin. For general reviews of flame excitation processes, see, e.g. Alkemade and Zeegers<sup>68a</sup> and Sugden.<sup>69</sup> For general discussions of flame emission methods the reader is referred to Refs. 68-73.

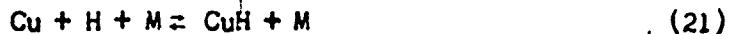
Extensive studies have been performed in the burned gases of  $C_xH_y/O_2$  and  $H_2/U_2$  flames with or without added diluents. Little "natural" emission from these gases occurs in the uv and visible part of the spectrum; as a result emission due to additives can readily be studied. Chemiluminescence is the dominant emission mechanism at "low" temperatures, achieved e.g. by heavy admixture of diluent; increasing temperature favors collisional excitation. The definition of low temperature in this connection varies with excitation energy. Sugden et al<sup>74</sup> estimate that for excitation of 600 nm radiation, collisional effects predominate above 1900 K, while emissions at 300 nm become primarily collisional only at temperatures above 2300 K.<sup>†</sup> In these burned gas mixtures H, OH and O are the principal naturally-occurring radicals. H and OH are in equilibrium with each other via



Since the equilibrium constant for this reaction and the  $[H_2]$  and  $[H_2O]$  at equilibrium are known, determination of the concentration of one of these reactants suffices for the determination of both. Padley and Sugden<sup>76</sup> added small quantities of Na to fuel-rich  $H_2/O_2/N_2$  flames and monitored the Na D-line emission resulting from



The emission intensity is proportional to  $[H]^2$ ;  $[H]$ -profiles thus obtained agree well with those observed by the CuH method.<sup>77</sup> The latter can also be used at high temperatures and is based on the equilibrium



and the accompanying CuH (0,0) 428.8 nm emission. Rosenfeld<sup>78</sup> has used the Pb equivalent of Reaction (20) at temperatures down to 1350 K. The  $[H]$ -profiles obtained in such studies have made it possible to measure the heat of dissociation of a large number of metal oxides and hydroxides in flames.<sup>56b,69</sup> It should be emphasized that Reaction (18) is a practical method for  $[H]$ -determination in O-atom lean flames. In O-rich flames the faster reaction



dominates.<sup>79</sup>

<sup>†</sup> This statement should not be construed to indicate that no chemiluminescence can be observed in flames at high temperatures. For example, Bulewicz<sup>75</sup> has found strong indications that most visible and ultraviolet emission from the primary reaction zone of some sub-atmospheric  $C_2N_2/O_2$  flames, in which temperatures in excess of 4000 K are obtained, is attributable to chemiluminescence.

In addition to this type of kinetic/thermochemical study, the secondary reaction zone of premixed hydrocarbon or  $H_2$  flames is also widely used in emission flame spectrophotometry applied to analytical chemistry. This type of analysis generally yields no information on the kind of chemical compound being analyzed but rather on the elements present in these compounds. It is primarily a quantitative (and qualitative) analysis method for metallic compounds present in liquid samples which may be delivered to the flame by a variety of means (see Alkemade<sup>70a</sup> for details). At the temperatures used the atomic line emissions observed are often the result of collisional excitation. However, chemiluminescence can be made to be the dominant metal atom excitation source using the other major burner type for this sort of work, the turbulent diffusion type burner.<sup>70a</sup> Unlike premixed flames at atmospheric pressure where the primary reaction zone is very thin, in turbulent diffusion flames primary combustion reactions can occur over several cm. By using a  $C_2H_2$  flame, or introducing the sample with an organic solvent into an  $H_2$  flame, intensity increases several orders of magnitude over the thermal equilibrium intensity have been obtained for many metallic lines.<sup>80</sup> This chemi-excitation is apparently related to the formation of the energetic (11.1 eV) CO bond,<sup>68,72a,80</sup> which is also thought to be responsible for most of the prominent natural chemiluminescence features of organic flames,<sup>81</sup> i.e.  $CH$ ,  $CHO$ ,  $CO$  and  $OH$ .

While not yet much exploited for quantitative analysis many emission bands of compounds formed in flames from metallic<sup>69,82</sup> and non-metallic<sup>70b</sup> elements have been observed, many of which are probably chemiluminescent in origin (for a compendium of such emissions see Pearse and Gaydon<sup>83</sup>). Examples of the utilization of such chemiluminescent emissions include measurements of gaseous samples of sulfur and phosphorus compounds with the Brody-Chaney  $H_2/O_2$  flame photometer. In the class of photometers to which this device belongs, the secondary zone is chilled to reduce the background emission.<sup>70b</sup> This is achieved by the use of a chimney (like a Smithells separator). The Brody-Chaney instrument was originally developed as a detector for gas chromatographic analyses and has now also been applied to direct sampling of air pollutants (see further Section III). In flame kinetic studies the  $NO/O$  continuum (Reaction 4) is widely used to measure  $[O]$  and/or  $[NO]$ .<sup>69,74</sup> The uv-visible ( $\lambda \geq 210$  nm)  $CO/O$  continuum<sup>68a,73</sup> is similarly used for  $[O]$  and/or  $[CO]$ .

Chemiluminescence may also be used in a very different manner to determine concentrations of reaction intermediates or other unstable species in high temperature environments, i.e. by the use of chemical scavenger probes. In such continuous flow probes, the sampled gases are expanded adiabatically (or cooled otherwise) to freeze the composition. A scavenger gas is introduced immediately downstream from the sample inlet to form stable products which can then be analyzed. Fristrom and Westenberg<sup>84</sup> used the  $O/NO_2$  titration

(Reaction 5) in this manner to determine  $[O]$  from flame gases; although they used mass spectrometric detection, chemiluminescence could probably have been used equally well. This was in fact done for N atoms via the N/NO titration (Reaction 15) by Fontijn, Rosner and Kurzius<sup>85</sup> who sampled from a supersonic plasma jet.

In shock tubes--the other major device for high temperature kinetic studies--a number of chemiluminescent reactions have been observed and used. The intensity of the uv  $O_2$  Schumann-Runge system ( $B^3\Sigma_u^- - X^3\Sigma_g^-$ ) due to the two-body radiative pre-association reaction



is proportional<sup>86,87</sup> to  $[O]^2$  and has been used to study C-atom reactions.<sup>88</sup> Such pre-association reactions are of an endothermic nature.<sup>89</sup> Reaction (23) has been used at temperatures above 2500 K where it leads to strong emission. By contrast, Reaction (17) which near room temperature gives rise to the weak Herzberg bands in the same wavelength region has (as a typical three-body reaction) a negative temperature dependence and contributes negligibly<sup>86</sup> in high temperature environments. Wray and Fried<sup>90</sup> using an atmospheric pressure arc have demonstrated that the emission from (23) is a discrete spectrum and that the spectral distribution is in accord with equilibrium theory. The emission can therefore also be used to determine reaction temperatures. The  $B^3\Sigma_u^- - X^3\Sigma_g^-$  emission from the S-atom equivalent of Reaction (23)



can be used in a similar manner for kinetic studies (and presumably for temperature determinations).<sup>91</sup> The radiative association of ground-state chlorine atoms gives rise to emission from the  $Cl_2^1\Pi_u$  and  $^3\Pi_{g,u}^+$  states,<sup>92</sup> which has been used to study the rate of  $Cl_2$  dissociation behind shock waves.<sup>93</sup> Some other chemiluminescent reactions used in shock tube studies are the  $CO_2$  continuum, due to the  $O + CO + M$  reaction, for which<sup>94</sup>  $I \propto [O][CO]$ , the OH 306.4 nm system, due to the  $O + H + [M]$  reaction, for which<sup>95</sup>  $I = [O][H]$  and other emissions typical of organic combustion reactions such as  $CH$ ,  $CHO$ ,  $C_2$ ,  $CO$  chemiluminescence. The latter emissions though not simply related to reactant concentrations have nonetheless proven quite helpful in unraveling combustion mechanisms in shock tubes and flames and atom reactions in flow tubes.<sup>81</sup>

In closing this section, mention should be made of the glow discharge shock tube. In this device a flow tube, such as discussed in Section II.A., is used in such a fashion that a shock wave can be fired through the glowing gas thus heating the gas mixture so that the temperature dependence of chemiluminescent reactions can be studied. The temperature range covered thus far with this apparatus is from about 300 to 3300 K. The temperature dependence of

the rate coefficients of Reactions (4), (11), (16), and (18) and the CO/O glow have been determined in this manner.<sup>29,45,46,96</sup>

### C. Flow Visualization and Supersonic Flow Studies

One of the implicit advantages of using transparent vessels in which to study reactions leading to chemiluminescence is that flow patterns can easily be observed, thereby verifying that good mixing and smooth laminar flow, required for many kinetic studies, is obtained. Flow visualization is also used in studying supersonic flows. In wind tunnel tests at pressures below a few Torr, Schlieren photography is no longer practical for obtaining density variations around fixed objects.<sup>97a</sup> Here, chemiluminescence, particularly the nitrogen afterglow, has been found to be a very useful technique.<sup>97b</sup> Nitrogen is subjected to an electrical discharge before expansion through a nozzle and the shock waves around objects can readily be photographed.

The fluid dynamics of wakes and trails behind planetary atmospheric entry bodies has been studied in ground-based laboratories by shooting  $\approx 1$  cm diam spheres at  $\approx 6$  km sec $^{-1}$  through air at reduced pressures. Temperatures in the shock layers around these spheres are typically on the order of 6000-8000 K. As the gas expands around the body into the wake, its temperature decreases but its chemical composition relaxes relatively slowly, thus creating concentrations of atoms in excess of equilibrium and setting up conditions for chemiluminescence to occur. While the shock layer radiation is essentially thermal, the radiation from the wake is chemiluminescent in origin and consists of the O<sub>2</sub> Schumann-Runge Bands (Reaction 23), the air afterglow NO<sub>2</sub> continuum (Reaction 4), the NO  $\beta$ ,  $\gamma$  and  $\delta$  Bands, the O<sub>2</sub> Herzberg and Atmospheric Bands and the N<sub>2</sub> First Positive Bands (Reactions 16-18). The emissions and their intensities depend on the flux of chemically active species into the (turbulent) wakes (i.e. the mixing rates with ambient air), local temperatures and the rates of those reactions which deplete the chemically active species. Models describing the wake chemistry and fluid mechanics have been tested by comparing calculated emission properties with measured properties.<sup>98-100</sup> Emission from the relatively hot near wake is dominated by the strongly temperature-dependent O<sub>2</sub> Schumann-Runge Bands which last for several hundred body diameters.<sup>99</sup> At larger distances (the far wake) the O/NO air afterglow reaction emission dominates and has been used for verifying models.<sup>100</sup>

High speed entry bodies are subject to considerable heating and as a result, evaporation (ablation) from their surfaces occurs. The rate of such evaporation depends on the chemical composition of the body's exposed surface. Experimental studies have been performed to verify flow models taking into account large rates of evaporation ("massive blowing").<sup>101,102</sup> Objects of various configurations have

been placed in arc tunnels, with a stream of O atoms impinging upon them. The objects have a porous surface through which NO is injected. The streamlines separating the blown gas from the on-coming stream are readily visualized by emission from O/NO (Reaction 4).

Upper-atmospheric NO releases<sup>103</sup> have been simulated in a low density wind tunnel. A free jet of NO is injected into a super-sonic flow containing O atoms and the so-called headglow is generated. The O-atom flux is determined by titrating O with NO<sub>2</sub> (Reaction 5) until the headglow is extinguished. The measured headglow intensity at known reactant fluxes is used to analyze atmospheric releases (see Section IV.A.1). The known O-fluxes can also be used to calibrate other upper atmospheric sampling devices such as mass spectrometers.<sup>104</sup>

### III. MONITORING OF AIR POLLUTANTS

The first application of chemiluminescence to monitoring of an air pollutant--detection of atmospheric O<sub>3</sub> by (heterogeneous) chemiluminescence<sup>105</sup>--was reported more than a decade past. Active interest in chemiluminescence as a method for monitoring air pollution dates from about 1968 and at present chemiluminescence monitors for O<sub>3</sub>, SO<sub>2</sub> and oxides of nitrogen (NO, NO<sub>2</sub> and NO + NO<sub>2</sub> = NO<sub>x</sub>) are being employed at a rapidly expanding rate.

The majority of detectors in practical use are based on homogeneous gas-phase chemiluminescence. Two types of such detectors may be distinguished. The ambient temperature detector employs the chemiluminescent reaction between the small molecule of interest, X, in air or in the exhaust gas, and a second reactant species, R, which is added in excess to the flow reactor. For the reactions used, the intensity of the chemiluminescence is directly proportional to the product of reactant concentrations,  $I = k[R][X]$ . Since the second reactant gas is normally in large excess and its concentration is constant, I is directly proportional to sample concentration,  $I = k'[X]$ . In the other type of detector, chemiluminescence resulting from reactions between atomic or molecular fragments produced from primary molecules introduced into a flame is observed in the secondary combustion zone. Flame chemiluminescence methods are generally less specific than room temperature methods and are more applicable to the detection of classes of compounds, e.g. nitrogen or sulfur compounds.

Chemiluminescence detectors have some common advantages and disadvantages for air pollutant monitoring. They inherently possess a high degree of sensitivity, specificity and simplicity. With the use of high gain, low dark current photomultiplier tubes, extremely low levels of chemiluminescent emission can be detected. Trace

concentrations are more readily detected in emission, in which a positive quantity is measured, than in absorption, in which concentration is proportional to a small differential quantity. In order for another molecule to be a positive interference in the chemiluminescence detection of X it must react with R, this reaction must produce chemiluminescence, and this chemiluminescence must overlap considerably with the spectral region in which X produces emission. Such interference would be a rare happenstance. A third body which quenches the excited state responsible for emission is a potential negative interference. In trace atmospheric detection, however, the predominant quenching agents are  $O_2$  and  $N_2$ , which do not vary in concentration.

Chemiluminescence detectors can be simple, compact and constructed from commercially available components. The common components of the detectors include (i) the flow train--gas inlet system, flow meters, reaction chamber, and sample pump, and (ii) the electronics--a photomultiplier tube closely coupled to the reaction chamber through an optical filter (if needed), photomultiplier high voltage supply and amplifier and an analog read-out.

A limitation of chemiluminescence detection is that not all pollutants participate in useable reactions. In common with all optical techniques absolute measurements are too difficult for routine use and instrument calibration is required.

#### A. Ozone

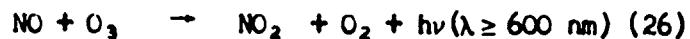
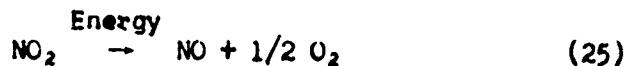
Regener<sup>105</sup> developed the first practical chemiluminescence  $O_3$  detector, which has been applied in both upper and lower atmospheric measurements. In Regener's procedure, the chemiluminescence obtained from the reaction between  $O_3$  and Rhodamine-B adsorbed on activated silica gel is measured as function of  $[O_3]$ . The technique is specific and is the most sensitive method known for  $O_3$ , with a lower limit of detection well below one part per billion (1 ppb). The Environmental Protection Agency (EPA) became interested in Regener's approach for routine detection of  $O_3$  in polluted atmospheres. Preliminary field studies were conducted in urban locations,<sup>106</sup> as a result of which preparation of the Rhodamine-B surface was modified to provide improved lifetime and stability.<sup>107</sup> The improved monitors have since shown excellent reliability in extended field studies<sup>108</sup> and form the basis for a commercially available monitor. The principal limitation of the Regener approach is the variable and slowly decaying sensitivity of the Rhodamine-B surface. An internal  $O_3$  source is necessary to provide frequent, periodic calibrations of the surface and compensate for any sensitivity changes. Although the internal calibration source works satisfactorily, a Regener-type instrument is more complicated than the homogeneous gas-phase chemiluminescence analyzers discussed below which have shown better response characteristics in comparative studies.<sup>109</sup>

In 1965, Nederbragt et al<sup>110</sup> published a note on the application of a homogeneous gas-phase chemiluminescence technique based on the atmospheric pressure chemiluminescent reaction between O<sub>3</sub> and C<sub>2</sub>H<sub>4</sub>. No information was available then on the mechanism of the reaction. The emission is a broad continuum centered near 435 nm and has been tentatively assigned to an excited aldehyde linkage (e.g. formaldehyde, glyoxal).<sup>109,111</sup> Scant attention was paid this technique until interest was revived by a 1970 investigation by Warren and Babcock.<sup>112</sup> Prototype detectors based on Nederbragt's concept were constructed and evaluated by EPA and were shown to have more than adequate sensitivity and specificity for ambient O<sub>3</sub> measurements.<sup>109</sup> In addition, the simplicity of the detector implied that a low cost monitor could be made. The Nederbragt method has been so successful in laboratory and field applications that it has been designated as the reference method for the routine O<sub>3</sub> measurements required by recent Federal air quality standards.<sup>113</sup> Several instrument companies now offer commercial versions. Good agreement has been obtained between Regener and Nederbragt O<sub>3</sub> monitors in extensive field studies.<sup>108,114-116</sup> In such field tests atmospheric data are collected with a variety of prototype and commercial units to determine reliability of instrument performance (e.g. downtime, maintenance requirements) and stability of instrument operating parameters (e.g. zero drift, span drift) and to compare data from different types of instruments.

The gas-phase chemiluminescent reaction between O<sub>3</sub> and NO may be used for the detection of either component when the other is present in excess.<sup>117</sup> For O<sub>3</sub> measurement the characteristics are essentially equivalent to those of the Nederbragt detector.<sup>109</sup> The reaction has been used almost exclusively for the measurement of NO and NO<sub>x</sub> as discussed below.

#### B. Nitrogen Oxides, Ammonia and Amines

Although oxides of nitrogen (NO<sub>x</sub>) play an important role in atmospheric pollution, methods of measuring NO<sub>x</sub> were until recently the least satisfactory among various atmospheric monitoring techniques. Chemiluminescent reactions of NO<sub>x</sub> have been adapted to fill this gap in measurement technology. The chemiluminescence system most frequently used is:



Reaction (26) is a red-shifted ( $\lambda \geq 600$  nm) modification of the air afterglow reaction (4).

Applications of gas-phase chemiluminescent reactions for detection of oxides of nitrogen were first discussed and experimentally demonstrated by Fontijn et al<sup>117</sup> at Aerchem under an EPA

contract. They subsequently constructed a prototype chemiluminescence NO monitor based on the  $\text{NO-O}_3$  reaction.<sup>115</sup> Sample air containing NO mixes with excess  $\text{O}_3$  (0.5% in  $\text{O}_2$  from an internal  $\text{O}_3$  source) in a reactor cell, which is maintained at a total pressure of approximately 2 Torr with a small mechanical pump. A thermoelectrically-cooled, infrared sensitive photomultiplier (e.g. EMI-9558A) and a filter cutting off radiation below 600 nm are closely coupled to the reactor vessel. The limit of sensitivity is approximately 0.002 ppm and the linear range of response extends up to 1000 ppm. Fontijn's prototype instrument, which is typical of many of the later commercial models, has been evaluated and compared with other  $\text{NO}_x$  instruments in extended field studies.<sup>114-116</sup>

The application of the chemiluminescent  $\text{NO-O}_3$  reaction has occupied several other investigators.<sup>119-121</sup> Prototype chemiluminescence NO monitors suitable for source and ambient measurements were developed independently at Ford Research Laboratories.<sup>119,120</sup> The chemiluminescence NO monitor has in fact proved to be an ideal method for measuring  $\text{NO}_x$  in automotive exhausts.<sup>121,122</sup> This technique is now specified by EPA as the test procedure for  $\text{NO}_x$  analytical measurements in determining whether vehicular emissions meet published standards.<sup>123</sup> Recently a chemiluminescence  $\text{NO-O}_3$  detector which operates at atmospheric pressure was demonstrated.<sup>124</sup> Sensitivity for ambient concentrations (0.001-1 ppm) was achieved by changing reactor geometry and sample flow conditions. This development has led to more compact and less costly detectors.

The means for carrying out Reaction (25) have occupied several investigators.<sup>121,124,125</sup> The initial studies were by Sigsby et al.,<sup>121</sup> who used a stainless steel tube heated to temperatures greater than 900 K and observed quantitative conversion of  $\text{NO}_2$  to NO. Thermal dissociation cannot account for this quantitative conversion and some contribution must be attributed to reduction of  $\text{NO}_2$  at the hot metal surface.  $\text{NH}_3$  can be oxidized to NO at high temperatures and is a potential interference since it is present in the atmosphere and may be present in certain sources. Acidic scrubbers which quantitatively remove  $\text{NH}_3$  and pass  $\text{NO}_2$  have been used.<sup>121,124</sup> Breitenbach and Shelef<sup>125</sup> have described a number of carbon impregnated metals which may be operated at two different temperatures for the conversion of  $\text{NO}_2$  or  $\text{NO}_2 + \text{NH}_3$  and recommended a carbon-molybdenum composite heated to 750 K. Application of such converters has not yet been reported.

When a converter is used  $\text{NO}_2$  concentrations can be determined by difference from the  $\text{NO}_x$  and NO measurements. For the direct measurement of  $\text{NO}_2$  a "photofragment" technique has been used. In this detector  $\text{NO}_2$  is photolyzed and the resulting O atoms are measured via Reaction (4), by addition of excess NO.<sup>126</sup> For concentrations below 1 ppm (ambient air concentrations) the response is linear, with a lower limit of detection of 1 ppb.

$\text{NH}_3$  is a constituent of the atmosphere which is produced by natural processes and by man's activities. Measurements of atmospheric  $\text{NH}_3$  are of interest to determine its chemical fate and to assess the potential role of  $\text{NH}_3$  in photochemical air pollution. A pyrolytic converter and a phosphoric acid pre-scrubber have been used by Hodgeson et al<sup>124</sup> to measure non-urban  $\text{NH}_3$  concentrations from 0.001 to 0.01 ppm via  $\{ [\text{NH}_3] + [\text{NO}_x] \} - [\text{NO}_x]$ .

The use of the O/NO reaction (4) can be advantageous in applications such as most source emissions where only a total  $\text{NO}_x$  measurement is required. Since the O/NO emission falls partly in the visible region, less expensive photomultipliers may be used. The original work here was performed by Snyder and Wooten<sup>127</sup> of Monsanto under an EPA contract. Equivalent responses were obtained for NO and  $\text{NO}_2$  and the detector sensitivity was found to be a few parts per billion. However, the electrical discharge O-atom sources used yielded a fluctuating background O/NO signal and O concentration. These problems have hindered application of this reaction. Work on a thermal O source, which could be more useful, has been reported.<sup>128</sup>

Reaction (13) also appears practical for  $\text{NO}_x$  measurements. Although no ambient temperature applications of this reaction have been reported, Krost et al<sup>129</sup> have observed the characteristic H/NO chemiluminescence in the secondary combustion zone of an  $\text{H}_2$ -rich flame, into which nitrogen compounds ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ , organic amines) were introduced. By incorporating a near infrared interference filter (690 nm) between the flame chemiluminescent zone and a photomultiplier, a detector for gas-phase nitrogen compounds was developed. The chemiluminescence intensity has been found to be directly proportional to the total concentration of nitrogen compounds, and the lower limit of sensitivity was established as approximately 0.1 ppm.

### C. Sulfur Compounds

Atmospheric sulfur-containing pollutants include  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , organic sulfides and mercaptans, sulfuric acid and sulfates. Of these  $\text{SO}_2$  has been the major pollutant of concern in atmospheric measurements.  $\text{H}_2\text{S}$  and organic sulfur comprise the class of malodorous sulfur compounds in the localized pollution associated with the Kraft paper industry. Sulfuric acid and sulfates occur predominantly in the particulate form.

The only chemiluminescence approach which has been applied to date is a flame method, which is applicable to the detection of gas-phase sulfur compounds as a class. When sulfur compounds are burned in an  $\text{H}_2$  rich flame, a strong blue chemiluminescence is emitted. The emitting molecule is  $\text{S}_2(\text{B}^3\Sigma_u^-)$ , formed via S-atom recombination either directly (Reaction 24) or indirectly (energy

transfer).<sup>130,131</sup> Since two atoms are required, the intensity of the chemiluminescence is proportional to the square of the concentration of sulfur compound in the flame (for compounds containing only one sulfur atom). The original flame photometric detector (FPD) for sulfur compounds in air was revealed in a patent by Draeger.<sup>132</sup> A modified version by Brody and Chaney<sup>133</sup> has been incorporated in a commercial sulfur monitor which has found extensive application in atmospheric monitoring. The calibration and application of this monitor for detecting atmospheric concentrations of SO<sub>2</sub> has been discussed by Stevens et al.<sup>134</sup> The typical FPD uses as fuel a mixture of 200 cc/min of air and 200 cc/min H<sub>2</sub>. An inert diluent gas (N<sub>2</sub>, He) can be used to lower the flame temperature and the flame emission background (compare Section II.B). Since air already contains N<sub>2</sub>, additional inert gas is not added to the atmospheric flame detector. The primary combustion zone is recessed in a barrel which functions as a light shield. The photomultiplier views the (cool) secondary combustion zone through an interference filter which transmits only the strong band at 394 nm. Although the emission is detected above the flame, the background signal obtained is predominantly due to flame background and is an order of magnitude greater than the photomultiplier dark current.<sup>133</sup> Thus the detector performance and sensitivity are determined by the magnitude of the drift and noise associated with the flame background emission. These are in turn strongly affected by flame temperature and gas flow rates. The flame noise for a typical flame photometric detector is equivalent to an SO<sub>2</sub> concentration of approximately 0.005 ppm. Efforts are underway to improve the performance of the FPD by correlation techniques.<sup>135,136</sup> The correlation technique used involves viewing and comparing one or more S<sub>2</sub> emission peaks and adjacent background wavelengths.

Considerable effort has been expended to develop a flame photometric based system which is specific for individual sulfur compounds. The most successful approach for atmospheric monitoring is the gas chromatographic (GC)-system developed by Stevens et al<sup>137</sup> for the quantitative elution of the sub-ppm concentrations of sulfur compounds found in the atmosphere (SO<sub>2</sub>, H<sub>2</sub>S, simple mercaptans and organic sulfides). Commercial instruments based on the GC-FPD combination are now available.

Both FPD and GC-FPD instruments have been extensively evaluated in field studies.<sup>108,114,115</sup> One of the most important observations of these studies was the close agreement obtained between the total sulfur measurement obtained with the FPD and the specific measurement of SO<sub>2</sub> by the GC-FPD. These results confirm those of Stevens et al,<sup>137</sup> who concluded that for most applications SO<sub>2</sub> accounts for 90% or more of the total gaseous S.

Ambient temperature chemiluminescent reactions have been suggested for measurement of SO<sub>2</sub> and other sulfur compounds, but applications have not yet been reported. In addition to their work

on  $\text{NO}_x$  detection, Snyder and Wooten<sup>127</sup> investigated the use of O-atom chemiluminescence for the detection of  $\text{SO}_2$ . Reaction of  $\text{SO}_2$  and C atoms produces  $\text{SO}_2$  chemiluminescence in the ultraviolet via<sup>138</sup>



The sensitivity obtained for  $\text{SO}_2$  detection using this chemiluminescence was 0.001 ppm, which is quite adequate for atmospheric detection. Since potential interfering molecules are known to produce chemiluminescence with O atoms in the ultraviolet, an interference filter is required to select a region of the  $\text{SO}_2$  chemiluminescence spectrum. As is the case with  $\text{NO}_x$  measurements, problems with O-atom sources have hindered development of a chemiluminescence  $\text{SO}_2$  detector. The use of thermal O-atom sources may stimulate practical developments.

Finally, Kummer, Pitts and Steer<sup>139</sup> have observed chemiluminescence from the gas-phase reactions of  $\text{O}_3$  with a variety of sulfur compounds, including  $\text{H}_2\text{S}$  and organic sulfides, and suggested use of this chemiluminescence for measuring atmospheric sulfur. The emission observed from both  $\text{H}_2\text{S}$  and organic sulfides was due to electronically excited  $\text{SO}_2$ . Therefore the use of  $\text{O}_3$  as a second reactant gas should lead to a non-specific detector for gaseous sulfur compounds. Moreover, since the reaction rate of  $\text{O}_3$  with different sulfur compounds varies considerably, the sensitivity of such a detector would depend upon the compounds measured.

#### D. Carbon Monoxide and Phosphorus, Boron, Chlorine Compounds

The reaction between O and CO produces a weak chemiluminescence in the 300-500 nm range.<sup>140</sup> Comparison<sup>117</sup> to the  $\text{O}_3/\text{NO}$  reaction suggests a predicted limit of sensitivity of 1 ppb. A preliminary study<sup>127</sup> was not successful but further investigation appears warranted.

In addition to measuring sulfur and nitrogen compounds, flame chemiluminescence methods have been used for the detection of phosphorus,<sup>132,133</sup> boron<sup>141</sup> and halogen<sup>142</sup> compounds in air. HPO emission is observed in the 540 nm region when phosphorus compounds are burned; the sensitivity is in the sub-ppm range. Such detectors have been applied to the detection of phosphorus-containing pesticides. Boron compounds (used as catalysts in industrial applications and as high quality rocket fuels) are detected via  $\text{BO}_2$  emission near 550 nm;<sup>141</sup> this FPD method is sensitive to concentrations of less than 0.1 ppm in air. Gilbert<sup>142</sup> has developed a sensitive flame emission method for chlorine compounds, in which indium metal is placed in the flame barrel. The presence of a small amount of indium vapor in the secondary combustion zone results in an intense chemiluminescent emission from  $\text{InCl}$  whenever chlorinated compounds are introduced into the flame. Application of this technique to atmospheric analysis has not been reported.

#### IV. UPPER ATMOSPHERE APPLICATIONS

Chemiluminescent reactions in the upper atmosphere have been chiefly observed at heights above 90 km. The pressure at 90 km is about  $10^{-3}$  Torr and falls to about  $5 \times 10^{-7}$  Torr at 200 km. Here most of the solar ultraviolet radiation is absorbed, dissociating molecular oxygen into atomic oxygen. Since there are few three-body collisions, O does not appreciably recombine with O<sub>2</sub> to form O<sub>3</sub>, as is the case at lower altitudes. At about 105 km, the number density of O equals that of O<sub>2</sub>; at about 150 km, [O] = [N<sub>2</sub>]. At 200 km, the atmosphere is composed of 70% O, 29% N<sub>2</sub>, 0.2% O<sub>2</sub> and small quantities of He, Ar and H<sub>2</sub>.<sup>143</sup> Atomic O plays the major role in producing chemiluminescence, especially when electronic excitation is involved.

##### A. Artificial Chemiluminescence

Luminescent clouds are produced by releasing from a rocket-borne container a reactive chemical that interacts with an atmospheric constituent to produce chemiluminescence. Such clouds are confined to the 90-200 km region of the upper atmosphere. Below 90 km not only the absence of O, but also the rapid condensation of the released chemicals prevents the observation of chemiluminescence, although it is possible to produce solar resonance excitation of atomic Na and Li as low as 80 km, and one can observe solar ray scattering from smoke trails at still lower altitudes. Above 200 km the released chemicals diffuse too rapidly to produce observable chemiluminescence. However, resonance fluorescence<sup>†</sup> of Na, released from a Soviet Sputnik<sup>144</sup> has been observed at 156,000 km altitude, and of Ba ions, released in a joint US-German rocket experiment, at 32,000 km.<sup>145</sup>

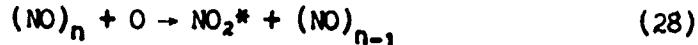
The artificial glow clouds or trails are photographed against a star background in the night or twilight sky. Time lapse photography allows measurement of drift velocity; thus, the horizontal and vertical components of the wind vectors can be established.<sup>146</sup> Up to about 110 km the clouds develop turbulent eddies and motions; above this altitude the clouds usually grow by molecular diffusion. Hence, eddy and molecular diffusion coefficients can be obtained by measuring the rate of growth of chemiluminescent clouds.<sup>147,148</sup> Atmospheric density can be derived from the molecular diffusion rates (see e.g. Ref. 149). Atomic O concentrations can be deduced from the measurement of light intensity of relatively simple chemiluminescent processes, such as the NO/O glow (Reaction 4).<sup>150</sup> Other applications of artificial chemiluminescence include the simulation of luminescent phenomena associated with missile exhaust gases and natural airglow

<sup>†</sup> This paper deals with chemiluminescence; therefore the numerous rocket experiments in which solar excitation of atomic resonance lines or molecular fluorescence is observed will be mentioned only in passing.

processes. In the following, we shall discuss the release techniques, reaction mechanisms and data interpretation of those chemiluminescent release agents found most useful in upper atmospheric studies. Doubtlessly, the ingenious atmospheric chemist will generate further ideas for suitable release chemicals and applications of chemiluminescent reactions for investigating this important region of the atmosphere.

1. Nitric Oxide. The air afterglow reaction was an obvious first choice for generating artificial chemiluminescence at night in the upper atmosphere. The first successful release of NO occurred in 1956.<sup>151</sup> This was a "point" release in which the NO was vented instantaneously by rupturing the container with a high explosive at 106 km altitude. An intense glow immediately appeared at the release point, growing in size and diminishing in intensity until 10 min after release when it was no longer observable. The second series of NO releases occurred in 1962.<sup>152</sup> The gas was released from a high pressure container through two sideward pointing ori-fices by opening a squib valve at 90 km altitude till the gas supply was exhausted at about 150 km. Here an unexpected effect was noticed. A bright annular headglow surrounded the rocket as it tra-versed the sky, followed by a much dimmer afterglow. The afterglow was observed for only about 100 sec after rocket passage in the 90 to 120 km region where it followed the ambient wind and turbulent motions. Both the headglow and afterglow showed a spectrum similar to the laboratory NO/O reaction.<sup>19</sup> Analysis of the headglow bright-ness revealed that with reasonable values for atomic O densities the volumetric emission rate exceeded by 3-4 orders of magnitude the expected emission rate from the normal three-body reaction (4).

Fontijn and Rosner have plausibly explained the anomalous intensity.<sup>153</sup> During the adiabatic expansion, the temperature of the NO drops rapidly and the saturation curve is passed. Therefore, it is expected that part of the gas forms molecular clusters and possibly, condensed particles. Before entering the mixing zone, the NO passes through a shock wave in which the temperature of the gas is nearly restored to the reservoir value. It is probable, how-ever, that some of the clusters survive the shock wave. The reaction then can be described as follows:



Here, the third body required in the normal three-body reaction (4) is carried along with the NO, so that basically every collision with atomic O could yield a stabilized  $NO_2^*$ . Therefore, NO clusters could account for the anomalously high photon emission rate pro-vided there is sufficient concentration of clusters in the mixing zone. Subsequently, wind tunnel simulation experiments by Golomb and Good<sup>154</sup> demonstrated that such clusters (of which the dimer is the simplest form) indeed exist in expanding NO jets and that there

is a direct relationship between cluster abundance in the free jet and photon emission rate in the headglow. Recently, it has also been shown that when the NO reservoir pressure,  $p_{NO}$ , multiplied by the release orifice diameter,  $d$ , exceeds a value of 100 Torr cm, the headglow intensity becomes independent of the NO flow rate and the total pressure in the mixing zone.<sup>150</sup> The brightness remains dependent, however, on the atomic O flux impinging onto the bow shock:

$$B = q n_0 \text{ photons cm}^{-2} \text{ sec}^{-1} \quad (30)$$

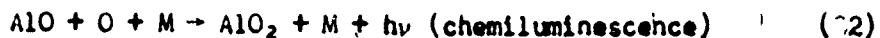
where  $n_0$  is the O flux (free stream O density multiplied by the stream velocity), and  $q$  is the efficiency factor by which photons are emitted per impinging O atom. This efficiency was determined to be  $q = 0.005$  with an uncertainty factor of 2.

Once the anomalous headglow intensity was explained, and the relevant efficiency factor determined in wind-tunnel calibrations, the NO release technique became a useful tool for upper atmosphere [O] determination.<sup>150</sup> In the rocket release, as in the wind-tunnel calibrations, the photometer is situated near the release orifice, viewing the headglow from its center. The measured brightness,  $B$ , is telemetered to the ground. From known vehicle velocity (which equals the stream velocity), ambient O densities are readily determined via Eq. (30). Current results are in good agreement with those derived from mass spectrometry.<sup>155</sup>

2. I trimethyl Aluminum (TMA). Woodbridge observed that aluminized grenades produce a long-lasting luminescence when exploded in the 100-125 km altitude region.<sup>156</sup> Rosenberg and Golomb proved that an aluminum compound must be involved.<sup>157</sup> They detonated two charges of high explosive at 114 km altitude, one containing Al powder as an additive, the other none. Only the aluminized charge produced luminescence. Rosenberg et al developed a more convenient method to release an aluminized compound in the upper atmosphere--TMA.<sup>158</sup> TMA is a pyrophoric liquid and its handling and loading require special care. Typically, the liquid is dispensed from a pressurized container along the rocket trajectory, starting at about 90 km. A part of the liquid flash-vaporizes upon release, the remainder freezes. The frozen particles follow the ballistic trajectory and evaporate upon re-entry into the denser regions of the atmosphere at 100-90 km. The flash-vaporized molecules react with some constituent of the atmosphere, presumably atomic O, since the glow is most intense where atomic O is most abundant. TMA produces no headglow, only an afterglow which takes several seconds to develop. The afterglow spectrum appears to be a continuum in the visible.<sup>159</sup> This glowing trail follows the ambient wind motions. It grows radially by eddy or molecular diffusion, respectively.

The following sequence of reactions appears most probable:





This scheme is in accord with the following observations. In the TMA clouds, about 0.3 to 0.6 photons are emitted per vaporized TMA molecule.<sup>158</sup> The high photon yield implies a cyclic process such as provided by Reaction (33) in which the intermediary molecule is regenerated. Fluorescence of the blue-green AlO bands ( $\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$ ) has been observed in twilight releases of TMA;<sup>159</sup> thus, the presence of AlO is established. From the fluorescence spectral intensity distribution atmospheric temperatures are now routinely deduced (see e.g. Ref. 160). The bond energy of AlO is about 5.1 eV,<sup>161</sup> about equal to that of O<sub>2</sub>, explaining the fact that AlO is not readily reduced to Al by atomic O. Most metal monoxides have bond energies smaller than D<sub>0</sub> O<sub>2</sub> and as a result do not persist in the O-rich region of the atmosphere, cf. e.g. FeO below.

3. Acetylene. C<sub>2</sub>H<sub>2</sub> has been released to simulate the luminous and radio-frequency effects observed following the passage through the upper atmosphere of hydrocarbon/liquid oxygen burning missiles.<sup>157</sup> C<sub>2</sub>H<sub>2</sub> probably comes closest to the hydrocarbon fragments and radicals found in missile exhausts. These fragments are believed to be responsible for the CH and C<sub>2</sub> band emission in missile plumes.<sup>162</sup> The highly energetic radicals may also enter into chemi-ionization reactions, causing the enhanced RF reflectivities of missile plumes at E-layer altitudes. The glow requires one to several seconds after release to develop. The spectrum is similar to that observed in the laboratory<sup>81</sup> and shows<sup>163</sup> an apparent weak continuum upon which are superimposed the CH 431.5 nm band (strong), the CH 389.0 nm band (weak), and the C<sub>2</sub> 516.5 nm band (weak). In addition there is a pronounced emission at about 577.0 nm [O(<sup>1</sup>S)  $\rightarrow$  O(<sup>1</sup>D)?]. Laboratory studies of the C<sub>2</sub>H<sub>2</sub>/O luminescence indicate that the CH bands become relatively more intense than the C<sub>2</sub> bands as pressure decreases.<sup>164</sup> The same effect has been observed in the upper atmosphere.

4. Iron Pentacarbonyl. Fe(CO)<sub>5</sub> has been released both at night and in twilight, in the 100-150 km region.<sup>165</sup> In twilight, when the sun still illuminates the ascending rocket, the fluorescence of the FeO orange bands is clearly observed in the headglow surrounding the rocket. The headglow is of short persistence and evolves into an afterglow of different spectral characteristics. In a subsequent, as yet unpublished, experiment it has been proven that the twilight afterglow consists of resonance scattering by FeI atoms. At night, Fe(CO)<sub>5</sub> produces a bright glow streaking through the sky, with no afterglow at all. Because of the reddish tint of the headglow, it is probable that some FeO molecules are produced in the emitting state, leading to chemiluminescence. An important observation is that in twilight the FeO fluorescence quickly disappears, indicating that

this molecule is consumed in a fast reaction such as  $\text{FeO} + \text{O} \rightarrow \text{Fe} + \text{O}_2$ . This reaction is exothermic by  $\approx 0.9$  eV, and laboratory experiments indicate that it is very fast.<sup>166</sup>

5. Other Chemical Releases. Several chemicals cause weak chemiluminescence in the upper atmosphere which is insufficient to obtain good wind, diffusion or composition measurements; however, the resulting glows might be interesting for the elucidation of the reaction mechanisms involved. These chemicals are  $\text{CS}_2$ ,  $\text{NO}_2$  and  $\text{Pb}(\text{CH}_3)_4$ .  $\text{CS}_2$  shows intense  $\text{SO}_2$  afterglow emission in the laboratory,<sup>167</sup> but in the upper atmosphere it is barely photographable.<sup>167</sup> This is attributable to the two steps necessary to produce the glow,  $\text{CS}_2 + \text{O} \rightarrow \text{CS} + \text{SO}$ , followed by Reaction (11). Apparently the steady-state concentration of  $\text{SO}$  following the release of  $\text{CS}_2$  is insufficient for high photon fluxes. Similarly,  $\text{NO}_2$  requires a two-step mechanism (Reactions 5 and 4) to produce light. However, not all multistep reactions lead to weak emission in the atmosphere as demonstrated by the TMA and  $\text{C}_2\text{H}_2$  reactions. In the case of TMA, the strong chemiluminescence can be attributed to recycling of  $\text{AlO}$ ; for  $\text{C}_2\text{H}_2$  the actual emission steps are mainly<sup>61</sup> atom stripping and exchange reactions which tend to be much faster<sup>168</sup> than association reactions, such as (4). The weak chemiluminescence produced<sup>169</sup> by the release of  $\text{Pb}(\text{CH}_3)_4$  may be attributed to a reaction such as

$$\text{PbO} + \text{O} \xrightarrow{M} \text{PbO}_2 + \text{h}\nu.$$

#### B. Natural Chemiluminescence (Airglow)

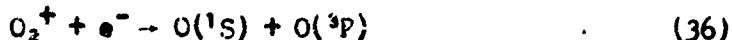
The many chemically highly active species (atoms, ions, free radicals and excited species) present in the undisturbed upper atmosphere give rise to a weak luminescent phenomenon, the airglow. The airglow can be observed from the ground, away from the interference of moon and star light and aurorae, as a diffuse omnipresent glow. Rocket and satellite measurements have considerably increased our knowledge of these glows and their origins. Chemiluminescent reactions are by far the dominant process of the night glows; in day glows chemiluminescence is much less important than radiative processes produced by solar irradiation. For general reviews of airglows and the excitation mechanisms involved, see e.g. Refs. 170-174. Known emission features which are thought to be mainly or in part due to chemiluminescence are<sup>170a</sup> the  $\text{O}_2(\text{A}^3\Sigma_u^+ - \text{X}^3\Sigma_g^-)$  Herzberg bands and  $(\text{b}^1\Sigma_g^+ - \text{X}^3\Sigma_g^-)$  atmospheric bands due to Reaction (17), the  $\text{NO}_2$  continuum due to the  $\text{O}/\text{NO}$  reaction (4), the  $\text{O}(\text{'S}-\text{'D})$  557.7 nm green line, the  $\text{Na}(2\text{p}-2\text{s})$  589.3 nm D line and the  $\text{OH}(v' \leq 9)$  vibration-rotation Meinel bands.

Some of the airglow measurement methods used or proposed are very similar to those employed in conjunction with the more intense artificial glows. A major difference from the latter is that in the natural glow one no longer has one known reactant concentration (i.e. that of the release agent). However observations of natural glows can be far more extensive in time and space which constitutes an important advantage.

Application to spatial isolation of the emitting layers and atmospheric dynamics is similar to the artificial glows and has been discussed (Sears,<sup>170b</sup> see also Silverman<sup>173</sup>). Temperature can be derived from several emission features. The Meinel OH bands are due to the reaction



Rotational equilibration requires only a few collisions and the rotational temperature of the Meinel bands is used as a measure of ambient temperature below about 90 km where collisions are sufficiently frequent.<sup>170c, 171a</sup> The O(<sup>1</sup>S) state has a radiative lifetime of 0.74 sec, orders of magnitude higher than the collision time at around 100 km, where a maximum in the intensity of the O(<sup>1</sup>S-<sup>1</sup>D) emission occurs, and the emitter at that altitude may therefore be considered to be thermalized; the Doppler line profile of this line is used as a measure of temperature.<sup>171a</sup> The O(<sup>1</sup>S) formation near 100 km is due to a reaction involving three O(<sup>3</sup>P) atoms (possibly via intermediate formation of an excited O<sub>2</sub> molecule). However, a second O-green line intensity maximum is observed near 180 km to which the reaction



contributes in a major way. Reaction (36) is 2.8 eV exothermic; since the only products are atomic species this energy must go into translational energy and as a result the emission profile is non-thermal at this higher altitude.<sup>171a</sup> Dandekar and Turtle<sup>175</sup> have measured the intensity of the oxygen green line with a rocket-borne photometer to determine the distribution of O(<sup>3</sup>P) as a function of altitude near 100 km. The results are in reasonable agreement with those measured by other means (mass spectrometry and NO releases).

In closing, it must be remarked that in view of the highly complex environment in which the natural airglows occur, measurements of these glows should be considered as very useful adjuncts to other upper atmospheric measurements rather than as supplying uniquely correct data. Agreement of results from various methods and their use in model atmospheres is leading to an ever more accurate knowledge of the upper atmosphere. It is likely that chemiluminescence is also going to play an important role in studying the upper atmosphere of other planets, once night glow observations of those environments are made.

## V. EPILOGUE

It may be concluded from this article that measurement techniques based on gas-phase chemiluminescence have found widespread use in the laboratory for reaction kinetics, quantitative analysis and gas dynamic studies. While there are several gaseous environments of major technological interest, applications of basic knowledge and laboratory techniques have thus far been mainly restricted to upper atmospheric studies and air pollutant monitoring. Recent rapid developments and acceptance of chemiluminescence techniques in this latter area suggest that similar developments may be possible elsewhere. Direct observations of practical combustion sources and monitoring and control of industrial process streams are examples of areas for which chemiluminescence techniques would appear to hold promise. A beginning along these lines is the study of NO formation in internal combustion engines via observation of the O/NO and O/CO continua by Lavoie, Heywood and Keck.<sup>176,177</sup> The advantages of chemiluminescence for monitoring process streams were pointed out a number of years ago<sup>178,179</sup> but no actual work along these lines has come to our attention, suggesting that this is still largely virgin territory.

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